

PTO 09-7505

CC = JP
20020426
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2002124297

NONAQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERY USING
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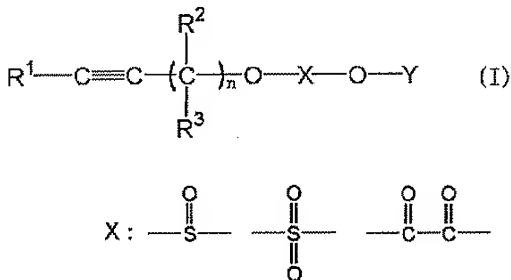
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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. SEPTEMBER 2009
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	2002124297
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	20020426
APPLICATION NUMBER	(21):	12313549
APPLICATION DATE	(22):	20001013
INTERNATIONAL CLASSIFICATION ⁷	(51):	H 01 M 10/40
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TITLE	(54):	NONAQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERY USING IT
FOREIGN TITLE	[54A]:	Hisui denkaieki oyobi sore o mochiita richiumu niji denchi

1. An electrolytic solution for a lithium secondary battery, wherein electrolytes are dissolved in a nonaqueous solvent, characterized by the following: it contains at least one type of alkyne derivative in said electrolytic solution, expressed by the following general formula (I):

[Structure 1]



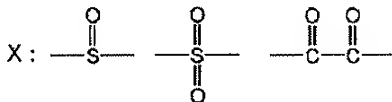
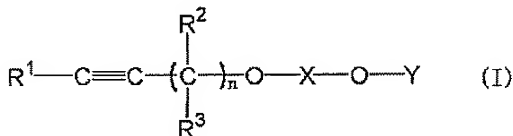
(where R^1 , R^2 and R^3 indicate, independently of one another, an alkyl group with 1-12 carbon atoms, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 atoms, an aralkyl group with 7-12 carbon atoms or a hydrogen atom. Moreover, R^2 and R^3 may bond with one another and form a cycloalkyl group with 3-6 carbon atoms. However, it should be noted that n is an integer of 1 or 2. In the formula, X indicates a sulfoxide group, a sulfone group or an oxalyl group; Y indicates an alkyl group with 1-12 carbon atoms, an alkenyl group, an alkynyl group, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 carbon atoms or an aralkyl group with 7-12 carbon atom.

2. A lithium secondary battery characterized by the following facts: the lithium secondary battery comprises a positive electrode, a negative electrode and an electrolytic solution wherein electrolytes are

* [Numbers in right margin indicate pagination of the original text.]

dissolved in a nonaqueous solution, and contains at least one type of alkyne derivative in said electrolytic solution, expressed by the following general formula (I)

[Structure 2]



(where R^1 , R^2 and R^3 indicate, independently of one another, an alkyl group with 1-12 carbon atoms, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 carbon atoms, an aralkyl group with 7-12 carbon atoms or a hydrogen atom. Moreover, R^2 and R^3 may bond with one another and form a cycloalkyl group with 3-6 carbon atoms. However, it should be noted that n is an integer of 1 or 2. In the formula, X indicates a sulfoxide group, a sulfone group or an oxalyl group; Y indicates an alkyl group with 1-12 carbon atoms, an alkenyl group, an alkynyl group, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 carbon atoms or an aralkyl group with 7-12 carbon atoms).

Detailed description of invention

[0001]

Technical background of the invention

The present invention relates to a novel electrolytic solution for a lithium secondary battery that can provide a lithium secondary battery with outstanding battery cycle properties and electrical capacity, storage properties and other battery properties as well as a lithium secondary battery using this.

[0002]

Prior art

In recent years, lithium secondary batteries have been used widely as a drive power source for small electronic devices and the like. Lithium secondary batteries are mainly configured of a positive electrode, a nonaqueous electrolytic solution and a negative electrode. In particular, a lithium secondary battery using LiCoO_2 and other lithium complex oxides as a positive electrode and a carbon material or lithium metal as a negative electrode is suitable for use. Thus, ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (MEC) and other carbonates are suitable for use as nonaqueous solvents for the electrolytic solution for the lithium secondary battery.

[0003]

Problems to be solved by the invention

However, there is a need for a secondary battery with outstanding battery cycle properties, electrical capacity and other battery properties. Lithium secondary batteries using LiCoO_2 , LiMn_2O_4 , LiNiO_2 and the like are such that the solvent in the nonaqueous electrolytic solution during charging is partially

oxidized and decomposed locally, and said decomposed substance brings about a decline in the battery performance which inhibits the desired electrochemical reaction for the battery. This is thought to originate in the electrochemical oxidation of the solvent on the surface of the positive electrode material and the nonaqueous electrolytic solution. Moreover, when lithium secondary batteries using a highly crystallized carbon material such as natural graphite or artificial graphite and the like are used as a negative electrode substance, peeling of the carbon negative electrode material is sometimes observed and the decrease in capacity is sometimes irreversible depending on the degree of the phenomenon. This peeling occurs when the solvent in the electrolytic solution is decomposed during charging and originates in the electrochemical reaction of the solvent on the surface of the carbon negative electrode material and the electrolytic solution. Here, an electrolytic solution that uses PC with a low melting point and a high dielectric constant has a high electric conduction even at low temperatures. However, when a graphite negative electrode is used, there are problems in that decomposition of the PC occurs and the battery performance declines. EC also presented problems in that part of it decomposed during repeated charging and discharging. As a result, the cycle properties of the battery and the electric capacity and other battery properties were by no means satisfactory.

[0004]

It is an objective of the present invention to solve the above problems relating to the electrolytic solution for a lithium secondary battery and to provide an electrolytic solution for a lithium secondary battery that can be used to configure a lithium secondary battery with outstanding battery cycle properties and outstanding electrical capacity and storage properties when charged and other battery properties, as well as a lithium secondary battery using this.

/3

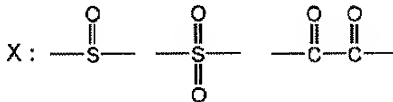
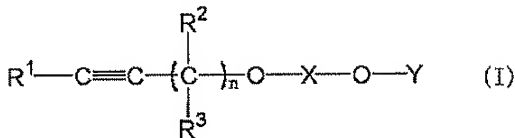
[0005]

Means to solve the problems

The present invention relates to an electrolytic solution, wherein electrolytes are dissolved in a nonaqueous solvent, for a lithium secondary battery, characterized by containing at least one type of alkyne derivative expressed by the following general formula (I) in said electrolytic solution:

[0006]

[Structure 3]



[0007]

(where R^1 , R^2 and R^3 indicate independently of one another an alkyl group with 1-12 carbon atoms, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 carbon atoms, an aralkyl group with 7-12 carbon atoms or a hydrogen atom. Moreover, R^2 and R^3 may bond with one another and form a cycloalkyl group with 3-6 carbon atoms. However, it should be noted that n is an integer of 1 or 2. In the formula, X indicates a sulfoxide group, a sulfone group or an oxalyl group; Y indicates an alkyl group

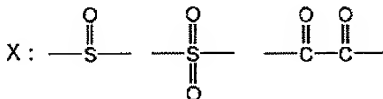
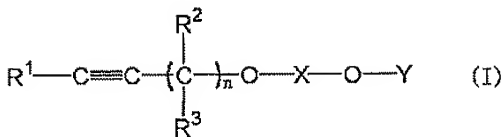
with 1-12 carbon atoms, an alkenyl group, an alkynyl group, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 carbon atoms or an aralkyl group with 7-12 carbon atoms).

[0008]

Moreover, the present invention relates to a lithium secondary battery, said lithium secondary battery comprising a positive electrode, a negative electrode and an electrolytic solution wherein electrolytes are dissolved in a nonaqueous solvent, characterized by containing at least one type of alkyne derivative in said electrolytic solution, and expressed by the following general formula (I):

[0009]

[Structure 4]



[0010]

(where R^1 , R^2 and R^3 indicate independently an alkyl group with 1-12 carbon atoms, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6 to 12 carbon atoms, an aralkyl group with 7-12 carbon

atoms or a hydrogen atom. Moreover, R^2 and R^3 may bond with one another and form an alkyl group with 3-6 carbon atoms. However, it should be noted that n is an integer of 1 or 2. In the formula, X indicates a sulfoxide group, a sulfone group, or an oxalyl group; Y indicates an alkyl group with 1-12 carbon atoms, an alkenyl group, an alkynyl group, a cycloalkyl group with 3-6 carbon atoms, an allyl group with 6-12 carbon atoms or an aralkyl group with 7-12 carbon atoms).

[0011]

The abovementioned alkyne derivative contained in the electrolytic solution is reduced and decomposed before the organic solvent in the electrolytic solution on the carbon negative electrode surface during charging. Part of said decomposed substance forms a passive state membrane on the surface of a highly crystallized active carbon negative electrode such as natural graphite or artificial graphite. As a result, it is assumed that reduction and decomposition of the organic solvent in the electrolytic solution can be prevented. Further, part of said decomposed substance oxidizes and decomposes before the organic solvent in the electrolytic solution on parts with micro-overvoltage wherein the electric potential of the surface of the positive electrode has increased excessively. It is assumed that oxidation and decomposition of the organic solvent in the electrolytic solution is prevented. As a result, it is thought to be effective in suppressing decomposition of the electrolytic solution without impairing the normal battery reaction.

[0012]

Effect of the invention

In the alkyne derivative expressed by the abovementioned general formula (I) and contained in the electrolytic solution in which electrolytes are dissolved in a nonaqueous solvent, R^1 , R^2 and R^3 should

be, independently of one another, a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group or other alkyl group with 1-12 carbon atoms. The alkyl group may be an isopropyl group, an isobutyl group or other branched alkyl group. Moreover, a cyclopropyl group, cyclohexyl group or other cycloalkyl group with 3-6 carbon atoms may be used. Further, a phenyl group, p-tolyl group or other allyl group with 6-12 carbon atoms, or a benzyl group, a phenethyl group or other aralkyl group with 7-12 carbon atoms may be contained. Moreover, R^2 and R^3 may bond with one another and form a cyclopropyl group bonded by 2-5 ethylene chains, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group or other cycloalkyl group with 3-6 carbon atoms. However, it should be noted that n is an integer of 1 or 2.

[0013]

Moreover, X in the alkyl derivative expressed in the abovementioned general formula (I) should be a sulfoxide group, a sulfo group or an oxalyl group. Further, Y should be a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group or other alkyl group with 1-12 carbon atoms. The alkyl group used may be an isopropyl group, an isobutyl group or other branched alkyl group. It may also be a cyclopropyl group, a cyclohexyl group or other cycloalkyl group with 3-6 carbon atoms. It may also be a phenyl group, a p-tolyl group or other aryl group with 6-12 carbon atoms. Further, it may contain a benzyl group, a phenethyl group or other aralkyl group with 7-12 carbon atoms. Moreover, Y may be a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group or other alkyl group with 1-12 carbon atoms; a vinyl group, an allyl group or other alkenyl group with 2-12 carbon atoms; a 2-propynyl group or a 3-butynyl group, a 1-methyl-2-propynyl group or other alkynyl group with 3-12 carbon atoms. Moreover, Y may be an alkynyl group with R^1 , R^2 and R^3 such that it is a symmetric compound with a center at X in general formula (I).

/4

[0014]

Specific examples of the alkyne derivative expressed by the abovementioned general formula (I) when X is a sulfoxide group are: di-(2-propynyl) sulfite ($R^1 = R^2 = R^3 =$ hydrogen atoms, Y = a 2-propynyl group, $n = 1$), di-(1-methyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, Y = a 1-methyl-2-propynyl group, $n = 1$), di-(2-butylnyl) sulfite ($R^1 =$ a methyl group, $R^2 = R^3 =$ a hydrogen atom, Y = a 2-butylnyl group, $n = 1$), di-(3-butylnyl) sulfite ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a 3-butylnyl group, $n = 2$), di-(2-pentylnyl) sulfite ($R^1 =$ an ethyl group, $R^2 = R^3 =$ a hydrogen atom, Y = 2-pentylnyl group, $n = 1$), di-(1-methyl-2-butylnyl) sulfite ($R^1 = R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, Y = a 1-methyl-2-butylnyl group, $n = 1$), di-(1,1-dimethyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ a methyl group, Y = a 1,1-dimethyl-2-propynyl group, $n = 1$), di-(1,1-diethyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ an ethyl group, Y = 1,1-diethyl-2-propynyl group, $n = 1$), di-(1-ethyl-1-methyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 =$ an ethyl group, $R^3 =$ a methyl group, Y = a 1-ethyl-1-methyl-2-propynyl group, $n = 1$), di-(1-isobutyl-1-methyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 =$ an isobutyl group, $R^3 =$ a methyl group, Y = a 1-isobutyl-1-methyl-propynyl group, $n = 1$), di-(1,1-dimethyl-2-butylnyl) sulfite ($R^1 = R^2 = R^3 =$ a methyl group, Y = a 1,1-dimethyl-2-butylnyl group, $n = 1$), di-(1-ethynyl cyclohexyl) sulfite ($R^1 =$ a hydrogen atom, R^2 and R^3 are a bonded pentamethylene group, Y = a 1-ethynyl cyclohexyl group, $n = 1$), di-(1-methyl-1-phenyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 =$ a phenyl group, $R^3 =$ a methyl group, Y = a 1-methyl-1-phenyl-2-propynyl group, $n = 1$), di-(1,1-diphenyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ a phenyl group, Y = 1,1-diphenyl-2-propynyl group, $n = 1$), methyl-2-propynyl sulfite ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a methyl group, $n = 1$), methyl-1-methyl-2-propynyl sulfite ($R^1 =$ a hydrogen atom, $R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, Y =

methyl group, $n = 1$), ethyl-2-propynyl sulfite ($R^1 = R^2 = R^3 =$ a hydrogen atom, $Y =$ an ethyl group, $n = 1$), phenyl 2-propynyl sulfite ($R^1 = R^2 = R^3 =$ a hydrogen atom, $Y =$ a phenyl group, $n = 1$), cyclohexyl 2-propynyl sulfite ($R^1 = R^2 = R^3 =$ a hydrogen atom, $Y =$ a cyclohexyl group, $n = 1$) and the like. However, it should by no means be construed that the present invention is restricted to these compounds.

[0015]

Specific examples of the alkyne derivative expressed by the abovementioned general formula (I) when X is a sulfone group are: di-(2-propynyl) sulfite ($R^1 = R^2 = R^3 =$ a hydrogen atom, $Y =$ a 2-propynyl group, $n = 1$), di-(1-methyl-2-propynyl) sulfite ($R^1 =$ a hydrogen atom, $R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, $Y =$ a 1-methyl-2-propynyl group, $n = 1$), di-(2-butylnyl) sulfate ($R^1 =$ a methyl group, $R^2 = R^3 =$ a hydrogen atom, $Y =$ a 2-butylnyl group, $n = 1$), di-(3-butylnyl) sulfate ($R^1 = R^2 = R^3 =$ a hydrogen atom, $Y =$ a 3-butylnyl group, $n = 2$), di-(2-pentylnyl) sulfate ($R^1 =$ an ethyl group, $R^2 = R^3 =$ a hydrogen atom, $Y =$ a 2-pentylnyl group, $n = 1$), di-(1-methyl-2-butylnyl) sulfate ($R^1 = R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, $Y =$ 1-methyl-2-butylnyl group, $n = 1$), di-(1,1-dimethyl-2-propynyl) sulfate ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ a methyl group, $Y =$ a 1,1-dimethyl-2-propynyl group, $n = 1$), di-(1,1-diethyl-2-propynyl) sulfate ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ an ethyl group, $Y =$ a 1,1-diethyl-2-propynyl group, $n = 1$), di-(1-ethyl-1-methyl-2-propynyl) sulfate ($R^1 =$ a hydrogen atom, $R^2 =$ ethyl group, $R^3 =$ a methyl group, $Y =$ a 1-ethyl-1-methyl-2-propynyl group, $n = 1$), di-(1-isobutyl-1-methyl-2-propynyl) sulfate ($R^1 =$ a hydrogen atom, $R^2 =$ an isobutyl group, $R^3 =$ a methyl group, $Y =$ a 1-isobutyl-1-methyl-2-propynyl group, $n = 1$), di-(1,1-dimethyl-2-butylnyl) sulfate ($R^1 = R^2 = R^3 =$ a methyl group, $Y =$ a 1,1-dimethyl-2-butylnyl group, $n = 1$), di-(1-ethynyl cyclohexyl) sulfate ($R^1 =$ a hydrogen atom, R^2 and R^3 are a bonded pentamethylene group, $Y =$ a 1-ethynyl cyclohexyl group, $n = 1$), di-(1-methyl-1-phenyl-2-propynyl) sulfate ($R^1 =$ a hydrogen atom, $R^2 =$ a phenyl group, $R^3 =$ a

methyl group, Y = 1-methyl-1-phenyl-2-propynyl group, n = 1), di-(1,1-diphenyl-2-propynyl) sulfate ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ a phenyl group, Y = a 1,1-diphenyl-2-propynyl group, n = 1), methyl-2-propynyl sulfate ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a methyl group, n = 1), methyl-1-methyl-2-propynyl sulfate ($R^1 =$ a hydrogen atom, $R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, Y = a methyl group, n = 1), ethyl-2-propynyl sulfate ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = an ethyl group, n = 1), phenyl-2-propynyl sulfate ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a phenyl group, n = 1), cyclohexyl-2-propynyl sulfate ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a cyclohexyl group, n = 1) and the like. However, it should by no means be construed that the present invention is restricted to these compounds. /5

[0016]

Specific examples of the alkyne derivative expressed by the abovementioned general formula (I) when X is oxalyl are: di-(2-propynyl) oxalate ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a 2-propynyl group, n = 1), di-(1-methyl-2-propynyl) oxalate ($R^1 =$ a hydrogen atom, $R^2 =$ methyl group, $R^3 =$ a hydrogen atom, Y = a 1-methyl-2-propynyl group, n = 1), di-(2-butynyl) oxalate ($R^1 =$ a methyl group, $R^2 = R^3 =$ a hydrogen atom, Y = 2-butynyl group, n = 1), di-(3-butynyl) oxalate ($R^1 = R^2 = R^3 =$ a hydrogen atom, Y = a 3-butynyl group, n = 2), di-(2-pentynyl) oxalate ($R^1 =$ an ethyl group, $R^2 = R^3 =$ a hydrogen atom, Y = a 2-pentynyl group, n = 1), di-(1-methyl-2-butynyl) oxalate ($R^1 = R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, Y = a 1-methyl-2-butynyl group, n = 1), di-(1,1-dimethyl-2-propynyl) oxalate ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ a methyl group, Y = a 1,1-dimethyl-2-propynyl group, n = 1), di-(1,1-diethyl-2-propynyl) oxalate ($R^1 =$ a hydrogen atom, $R^2 = R^3 =$ ethyl group, Y = a 1,1-diethyl-2-propynyl group, n = 1), di-(1-ethyl-1-methyl-2-propynyl) oxalate ($R^1 =$ a hydrogen atom, $R^2 =$ an ethyl group, $R^3 =$ a methyl group, Y = a 1-ethyl-1-methyl-2-propynyl group, n = 1), di-

(1-isobutyl-1-methyl-2-propynyl) oxalate (R^1 = a hydrogen atom, R^2 = an isobutyl group, R^3 = methyl group, Y = a 1-isobutyl-1-methyl-2-propynyl group, $n = 1$), di-(1,1-dimethyl-2-butynyl) oxalate ($R^1 = R^2 = R^3$ = a methyl group, Y = a 1,1-dimethyl-2-butynyl group, $n = 1$), di-(1-ethynyl cyclohexyl) oxalate (R^1 = a hydrogen atom, R^2 and R^3 are a bonded pentamethylene group, Y = a 1-ethynyl cyclohexyl group, $n = 1$), di-(1-methyl-1-phenyl-2-propynyl) oxalate (R^1 = a hydrogen atom, R^2 = a phenyl group, R^3 = a methyl group, Y = a 1-methyl-1-phenyl-2-propynyl group, $n = 1$), di-(1,1-diphenyl-2-propynyl) oxalate (R^1 = a hydrogen atom, $R^2 = R^3$ = a phenyl group, Y = a 1,1-diphenyl-2-propynyl group, $n = 1$), methyl-1-methyl-2-propynyl oxalate ($R^1 = R^2 = R^3$ = a hydrogen atom, Y = a methyl group, $n = 1$), methyl-1-methyl-2-propynyl oxalate (R^1 = a hydrogen atom, R^2 = a methyl group, R^3 = a hydrogen atom, Y = a methyl group, $n = 1$), ethyl-2-propynyl oxalate ($R^1 = R^2 = R^3$ = a hydrogen atom, Y = an ethyl group, $n = 1$), phenyl-2-propynyl oxalate ($R^1 = R^2 = R^3$ = a hydrogen atom, Y = a phenyl group, $n = 1$), cyclohexyl-2-propynyl oxalate ($R^1 = R^2 = R^3$ = a hydrogen atom, Y = a cyclohexyl group, $n = 1$) and the like. However, it should by no means be construed that the present invention is restricted to these compounds.

[0017]

For the abovementioned alkyne derivative, when the alkyne derivative expressed by the abovementioned general formula (I) is contained in excess, the electrical conductivity in the electrolytic solution changes and the battery performance declines. Moreover, when not enough is contained, a sufficient coating cannot be formed and the expected battery properties cannot be obtained. As a result, it should be 0.01-20 wt% and particularly 0.1-10 wt% relative to the amount of the electrolytic solution.

[0018]

The nonaqueous solvent used in the present invention may be ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), vinylene carbonate (VC) and other cyclic carbonates, γ -butyrolactone and other lactones, dimethyl carbonate (DMC), methyl ethyl carbonate (MEC), diethyl carbonate (DEC) and other chain carbonates, tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dibutoxyethane and other ethers, acetonitrile and other nitriles, methyl propionate, methyl pivalinate, octyl pivalinate and other esters, dimethyl formamide and other amides.

[0019]

These nonaqueous solvents may be used alone or as a combination of two or more types. There are no particular restrictions on the combination of nonaqueous solvents. However, a combination of cyclic carbonates and chain carbonates, a combination of cyclic carbonates and lactone carbonates and a combination of three types of cyclic carbonates and chain carbonates may be used.

[0020]

The electrolytic solution used in the present invention may be LiPF_6 , LiBF_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$, $\text{LiPF}_3(\text{CF}_3)_3$, $\text{LiPF}_3(\text{iso-C}_3\text{F}_7)_3$, $\text{LiPF}_3(\text{iso-C}_3\text{F}_7)$ and the like. One of these electrolytes or a combination of two or more of these electrolyte solutions may be used. These electrolytes should usually be dissolved at a concentration of 0.1-3 M and preferably 0.5-1.5M relative to the abovementioned nonaqueous solvents.

[0021]

The nonaqueous electrolytic solution in the present invention may be obtained by mixing the abovementioned nonaqueous solvent, dissolving the abovementioned electrolyte in this, and at least one type of these alkyne derivatives expressed by the abovementioned formula (I) may be dissolved.

[0022]

/6

The nonaqueous electrolytic solution in the present invention is used suitably as a constituent member of a secondary battery, particularly a constituent member of a lithium secondary battery. Although there are no particular restrictions on the constituent members other than the nonaqueous electrolytic solution making up the secondary battery, a variety of conventionally used constituent members may be used.

[0023]

For example, a composite metal oxide of lithium and at least one type selected from a group made up of cobalt, manganese, nickel, chromium, iron and vanadium and lithium is used as a positive electrode activated substance. Examples of this type of composite metal are: LiCoO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ ($0.01 < x < 1$) and the like. Moreover, LiCoO_2 and LiMn_2O_4 , LiCoO_2 and LiNiO_2 , LiMn_2O_4 and LiNiO_2 and the like may be mixed together and suitably used.

[0024]

The positive electrode is such that the abovementioned positive electrode activated substance, acetylene black, carbon black and other conducting agents, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), copolymers of styrene and butadiene (SBR), copolymers of

acrylonitrile and butadiene (NBR), carboxymethyl cellulose (CMC) and other bonding agents and solvents. Then, we coated this positive electrode material on an aluminum foil and stainless steel lath plate as a collector, allowed it to dry and pressure-molded it. Then, it was produced by heating for approximately 2 h in a vacuum at a temperature of approximately 50-250°C.

[0025]

A carbon material which can occlude and discharge a lithium metal, a lithium alloy or lithium (pyrocarbon, coke, graphite (artificial graphite, natural graphite and the like), an organic polymer compound combustion body, carbon fiber) or a composite tin oxide or other oxide is used as a negative electrode activated substance. A carbon material with a graphite type crystalline structure wherein the spacing (d_{002}) of the lattice plane (002) is 0.335-0.340 nm (nanometers) is particularly suitable. Furthermore, a powder material such as a carbon material is kneaded with an ethylene propylene-dienta-polymer (EPDM), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), copolymers of styrene and butadiene (SBR), copolymers of acrylonitrile and butadiene (NBR), carboxymethyl cellulose (CMC) and other binding agents and used as a negative electrode mixture.

[0026]

There are no particular restrictions on the structure of the lithium secondary battery. Examples are a coil battery or a polymer battery with a single-layer or multiple-layer positive electrode, negative electrode or separator. It may also be a cylindrical battery or angular battery with a roll-shaped positive electrode, negative electrode or roll-shaped separator. Moreover, a well-known polyolefin porous membrane, woven cloth, nonwoven cloth and the like may be used.

[0027]

Application examples

Next, we shall provide a specific explanation of the present invention by means of application and comparative examples.

Application Example 1

Preparation of Electrolytic Solution

We prepared a PC/DMC (capacity ratio) = 3/7 nonaqueous solvent, dissolved LiPF_6 in this so that the concentration was 1M and prepared the electrolytic solution. Then, we added di-(2-propynyl) sulfite (in general formula (I), $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{a hydrogen atom}$, $\text{X} = \text{a sulfoxide group}$, $\text{Y} = \text{a 2-propynyl group}$, $n = 1$) as an alkyne derivative to the electrolytic solution so that it was 0.5 wt%.

[0028]

Preparation of lithium secondary battery and measurement of battery properties

We mixed 80 wt% of LiCoO_2 (positive electrode activated substance), 10 wt% of acetylene black (conductive agent) and 10 wt% of polyvinylidene fluoride (binding agent). We added 1-methyl-2-pyrrolidone to this, made a slurry of it and coated it on aluminum foil. Then, we dried this and pressure-molded it, thereby preparing the positive electrode. We mixed 90 wt% of artificial graphite (negative electrode activated substance) and 10 wt% of polyvinylidene fluoride (binding agent). We added 1-methyl-2-pyrrolidone to this, made a slurry of it and coated it on copper foil. Then, we dried it and pressure-molded it, thereby producing the negative electrode. Then, we produced a coin battery (20 mm diameter, 3.2 mm thick) into which the abovementioned electrolytic solution had been injected using a polypropylene micropore film separator. We charged it to 4.2 V at room temperature (20°C) at a

constant current of 0.8 mA using this coin battery. Next, we discharged it at a constant current of 0.8 mA up to a final voltage of 2.7 V and repeated this charging. The initial discharge capacity was 0.98 and was calculated as the relative capacity compared to when 1M LiPF₆ + PC/EC/DEC (capacity ratio) = 5/25/70 was used as the electrolytic solution (Comparative Example 2). We measured the battery properties after 50 cycles and found that the discharge capacity maintenance rate was 90.1% when the initial discharge capacity was 100%. Moreover, the low-temperature properties were good. The production conditions as well as the battery properties are indicated in Table 1.

[0029]

Application Example 2

We produced a coin battery just as we did in Application Example 1, except that we used 2 wt% of di-(2-propynyl) sulfite for the electrolytic solution. We measured the battery properties and found that the relative capacity of the initial discharge capacity was 0.97. We measured the battery properties after 50 cycles and found that the discharge capacity maintenance rate was 90.7%. Moreover, the low-temperature properties were good. The production conditions as well as the battery properties of the coin battery are indicated in Table 1.

[0030]

Application Example 3

We produced a coin battery just as we did in Application Example 1, except that we used 5 wt% of di-(2-propynyl) sulfite relative to the electrolytic solution. We measured the battery properties and found that the relative capacity of the initial discharge capacity was 0.96. We measured the battery properties after 50 cycles and found that the discharge capacity maintenance rate was 90.5%. Moreover, the low-

temperature properties were also good. The production conditions as well as the battery properties for the coin battery are indicated in Table 1.

[0031]

/7

Application Example 4

We produced a coin battery just as we did in Application Example 1, except that we used 2 wt% of methyl 2-propynyl sulfate (in general formula (I), $R^1 = R^2 = R^3 =$ hydrogen atoms, Y = a methyl group, $n = 1$) as an alkyne derivative relative to the electrolytic solution. We measured the battery properties and found the relative capacity of the initial discharge capacity was 0.97. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate to be 89.8%. The low-temperature properties were good as well. The production conditions as well as the battery properties of the coin batteries are indicated in Table 1.

[0032]

Application Example 5

We produced a coin battery just as we did in Application Example 1 except that we used 2 wt% of di-(2-propynyl) oxalate (in general formula (I), $R^1 = R^2 = R^3 =$ a hydrogen atom, X = an oxalyl group, Y = a 2-propynyl group, $n = 1$) as an alkyne derivative relative to the electrolytic solution. We measured the battery properties and found the initial discharge capacity to be 0.97. We measured the battery properties after 50 cycles and found that the discharge capacity maintenance rate was 90.2%. The low-temperature properties were good as well. The production conditions and the battery properties for the coin battery are indicated in Table 1.

[0033]

Comparative Example 1

We prepared a nonaqueous solvent with a PC/DMC (capacity ratio) of 3/7 and dissolved LiPF_6 in this so that the concentration was 1M. At this time, none of the alkyne derivative had been added. We produced a coin battery just as we did in Application Example 1 using this electrolytic solution. We measured the battery properties and found no charging or discharging. The production conditions as well as the battery properties for the coin battery are indicated in Table 1.

[0034]

Application Example 6

We produced a nonaqueous solvent with a PC/EC/DEC (capacity ratio) of 5/25/70 and prepared an electrolytic solution by dissolving LiPF_6 in this so that the concentration was 1M. Then, we added 2 wt% of di-(1-methyl-2-propynyl) sulfite (in general formula (I), R^1 = a hydrogen atom, R^2 = a methyl group, R^3 = a hydrogen atom, X = a sulfoxide group, Y = a 1-methyl-2-propynyl group, $n = 1$) as an alkyne derivative relative to the electrolytic solution. We produced a battery just as we did in Application Example 1 using this electrolytic solution. The initial discharge capacity was 1.02 and was calculated as the relative capacity compared to when 1M LiPF_6 + PC/EC/DEC (capacity ratio) = 5/25/70 was used as the electrolytic solution (Comparative Example 2). We measured the battery properties after 50 cycles and found that when the initial discharge capacity was 100%, the discharge capacity maintenance rate was 92.2%. The production conditions and the battery properties for the coin battery are indicated in Table 1.

[0035]

Application Example 7

We produced a coin battery just as we did in Application Example 6, except that we used 2 wt% of methyl 2-propynyl sulfite (in general formula (I), $R^1 = R^2 = R^3 =$ a hydrogen atom, X = a sulfoxide group, Y = a methyl group, $n = 1$) as an alkyne derivative relative to the electrolytic solution. We measured the battery properties and found the relative capacity of the initial discharge capacity was 1.02. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate was 91.8%. The low-temperature properties were good as well. The production conditions and the battery properties of the coin battery are indicated in Table 1.

[0036]

Application Example 8

We produced a coin battery just as we did in Application Example 6, except that we used 2 wt% of di-(1-methyl-2-propynyl) oxalate (in general formula (I), $R^1 =$ a hydrogen atom, $R^2 =$ a methyl group, $R^3 =$ a hydrogen atom, X = an oxalyl group, Y = a 1-methyl-2-propynyl group, $n = 1$) as an alkyne derivative relative to the electrolytic solution. We measured the battery properties and found the relative capacity of the initial discharge capacity was 1.02. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate was 91.9%. The low-temperature properties were good as well. The production conditions and the battery properties of the coin battery are indicated in Table 1.

[0037]

Application Example 9

We produced a coin battery just as we did in Application Example 6, except that we used 2 wt% of methyl-2-propynyl oxalate (in general formula (I), $R^1 = R^2 = R^3 =$ a hydrogen atom, X = an oxalyl group, Y = a methyl group, $n = 1$) as an alkyne derivative relative to the electrolytic solution. We measured the battery properties and found the relative capacity of the initial discharge capacity was 1.03. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate was 91.1%. The low-temperature properties were good as well. The production conditions and the battery properties of the coin battery are indicated in Table 1.

[0038]

Application Example 10

We produced a coin battery by preparing an electrolytic solution just as we did in Application Example 6, except that we used 2 wt% of di-(2-propynyl) sulfite as an alkyne derivative using LiMn_2O_4 instead of the LiCoO_2 as a positive electrode activated substance. We measured the battery properties and found the relative capacity of the initial discharge capacity was 0.83. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate was 93.1%. The production conditions as well as the battery properties are indicated in Table 1.

[0039]

Application Example 11

We produced a coin battery by preparing an electrolytic solution just as we did in Application Example 6, except that we used 2 wt% of di-(2-propynyl) sulfite as an alkyne derivative relative to the

electrolytic solution using $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ instead of LiCoO_2 as a positive electrode activated substance. We measured the battery properties and found the relative capacity of the initial discharge capacity was 1.19. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate was 90.5%. The production conditions as well as the battery properties of the coin battery are indicated in Table 1.

[0040]

Application Example 12

We produced a coin battery by preparing an electrolytic solution just as we did in Application Example 6, except that we used 2 wt% of di-(2-propynyl) sulfite as an alkyne derivative relative to the electrolytic solution using natural graphite instead of artificial graphite as a negative electrode activate substance. We measured the battery properties and found the relative capacity of the initial discharge capacity was

/8

1.02. We measured the battery properties after 50 cycles and found the discharge capacity maintenance rate was 93.2%. The production conditions as well as the battery properties of the coin battery are indicated in Table. 1.

[0041]

Comparative Example 2

We prepared a PC/EC/DEC (capacity ratio) = 5/25/70 nonaqueous solvent and dissolved LiPF_6 in this so that the concentration was 1M. None of the alkyne derivative whatsoever was added at this time. We produced a coin battery just as we did in Application Example 6 using this electrolytic solution. We

measured the battery properties and found the discharge capacity maintenance rate was 81.8%. The production conditions as well as the battery properties of the coin battery are indicated in Table 1.

[0042]

TABLE 1

	①	②	③	④	⑤	⑥	⑦
	正極	負極	化合物	添加量 wt%	電解液組成 (容量比)	初期放 電容量 (相対 値)	50 サ イクル 放電容 量維持 率%
⑧ 実施例 1	LiCoO ₂	⑩ 人造黒鉛	ジ(2-プロピニル)サル ファイト ⑫	0.5	1M LiPF ₆ PG/DWC=3/7	0.98	90.1
実施例 2	LiCoO ₂	人造黒鉛	ジ(2-プロピニル)サル ファイト ⑫	2	1M LiPF ₆ PG/DWC=3/7	0.97	90.7
実施例 3	LiCoO ₂	人造黒鉛	ジ(2-プロピニル)サル ファイト ⑫	5	1M LiPF ₆ PG/DWC=3/7	0.98	90.5
実施例 4	LiCoO ₂	人造黒鉛	メチル 2-プロピニル サルファイト ⑬	2	1M LiPF ₆ PG/DWC=3/7	0.97	89.8
実施例 5	LiCoO ₂	人造黒鉛	ジ(2-プロピニル)オギ ザレート ⑭	2	1M LiPF ₆ PG/DWC=3/7	0.97	90.2
⑨ 比較例 1	LiCoO ₂	人造黒鉛	なし ⑮	0	1M LiPF ₆ PG/DWC=3/7	0	⑩ 充放電 しない
⑧ 実施例 6	LiCoO ₂	人造黒鉛	ジ(1-メチル-2-プロピ ニル)サルファイト ⑯	2	1M LiPF ₆ PG/EC/DEC=5/25/70	1.02	92.2
実施例 7	LiCoO ₂	人造黒鉛	メチル 2-プロピニル サルファイト ⑰	2	1M LiPF ₆ PG/EC/DEC=5/25/70	1.02	91.8
実施例 8	LiCoO ₂	人造黒鉛	ジ(1-メチル-2-プロピ ニル)オギザレート ⑱	2	1M LiPF ₆ PG/EC/DEC=5/25/70	1.02	91.9
実施例 9	LiCoO ₂	人造黒鉛	メチル 2-プロピニル オギザレート ⑫	2	1M LiPF ₆ PG/EC/DEC=5/25/70	1.03	91.1
実施例 10	LiMn ₂ O ₄	人造黒鉛	ジ(2-プロピニル)サル ファイト ⑫	2	1M LiPF ₆ PG/EC/DEC=5/25/70	0.83	93.1
実施例 11	LiCoO ₂ NiFeO ₂	人造黒鉛	ジ(2-プロピニル)サル ファイト ⑫	2	1M LiPF ₆ PG/EC/DEC=5/25/70	1.19	90.5
⑪ 実施例 12	LiCoO ₂	⑪ 天然黒鉛	ジ(2-プロピニル)サル ファイト ⑫	2	1M LiPF ₆ PG/EC/DEC=5/25/70	1.02	93.2
⑨ 比較例 2	LiCoO ₂	人造黒鉛	なし ⑮	0	1M LiPF ₆ PG/EC/DEC=5/25/70	1	81.8

Key:	1	Positive electrode
	2	Negative electrode
	3	Compound
	4	amount added wt%
	5	Electrolytic solution composition (capacity ratio)
	6	Initial Discharge Capacity (relative capacity value)
	7	50-cycle Discharge Capacity Maintenance Rate%
	8	Application Example __
	9	Comparative Example __
	10	Artificial graphite
	11	Natural graphite
	12	Di-(2-propynyl) sulfite
	13	Methyl 2-propynyl sulfate
	14	Di-(2-propynyl)oxalate
	15	None
	16	Di-(1-methyl-2-propynyl) sulfate
	17	Di-(1-methyl-2-propynyl) oxalate
	18	Methyl 2-propynyl oxalate
	19	Application Example 9 / LiCoO_2 / artificial graphite /
	18	Application Example 10 / LiMn_2O_4 / artificial graphite / di-(2-propynyl) sulfite
	19	No charging or discharging

[0043]

Furthermore, it should by no means be construed that the present invention is restricted to these application examples, and a variety of combinations can be easily made based on the gist of the present invention. There are no particular restrictions on these combinations. Further, the abovementioned practical examples relate to a coin battery, however, the present invention is also applicable to a cylindrical battery or an angular battery.

[0044]

Effect of the invention

The present invention provides a lithium secondary battery with outstanding cycle properties and electrical capacity within a wide range as well as outstanding storage properties and battery properties.